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**EP-A- 0 204 432 EP-A- 0 313 904**  
**EP-A- 0 358 933 FR-A- 2 546 159**  
**GB-A- 2 106 891 US-A- 2 278 867**

**CHEMICAL ABSTRACTS, vol. 110, no. 10, May 15, 1989, Columbus, Ohio, US; abstract no. 178391F, page 329**

**CHEMICAL ABSTRACTS, vol. 97, no. 22, February 1982, Columbus, Ohio, US; abstract no. 187053N, page 303**

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## Description

This invention relates to glass flux compositions for use in enamels and cover flux coatings.

Many different ingredients in many different concentrations in many different combinations are known in glass flux compositions in order to provide the properties desired. Such fluxes are admixed with pigments to make enamel compositions to decorate articles. Alternatively, such fluxes are dispersed in carrier materials to make cover flux compositions for application to articles to give them a protective coating. A surprisingly useful new flux composition has now been discovered.

Lead is widely used as a major constituent of enamels. There is concern, however, at the possibility of lead being leached out of enamels on articles, for instance from containers in contact with food. Accordingly, the invention provides a replacement which is not based on the use of lead in the formulations.

US specification 4340645 discloses a ceramic frit which when smelted consists essentially of:

- (a) from 4.0 to 6.5 wt% of a compound selected from the group consisting of potassium oxide, sodium oxide, lithium oxide, and mixtures thereof;
- (b) from 7.0 to 12.5 wt% of zinc oxide;
- (c) from 7.0 to 12.0 wt% of calcium oxide;
- (d) from 0 to 0.7 wt% of magnesium oxide;
- (e) from 0 to 5.0 wt% of barium oxide;
- (f) from 2.0 to 4.0 wt% of strontium oxide;
- (g) from 2.5 to 6.0 wt% of boric oxide;
- (h) from 7.0 to 8.5 wt% of aluminium oxide;
- (i) from 54.0 to 60.0 wt% of silica;
- and
- (j) from 0 to 1.0 wt% of zirconium oxide; all said wt% being based on the total weight of all of said components (a) through (j).

GB specification 2115403A discloses an optical and ophthalmic glass with a refractive index greater than or equal to 1.56, an Abbe number greater than or equal to 40 and a density of less than or equal to 2.70g/cm<sup>3</sup>, having the following composition in wt%:

30	$\text{SiO}_2$	47	to	75
	$\text{B}_2\text{O}_3$	1	to	20
	$\text{Al}_2\text{O}_3$	0	to	10
35	$\text{P}_2\text{O}_5$	0	to	5

the sum of

40	$\text{SiO}_2, \text{B}_2\text{O}_3, \text{Al}_2\text{O}_3 \text{ and } \text{P}_2\text{O}_5$			
		57	to	85
45	$\text{Li}_2\text{O}$	0	to	15
	$\text{Na}_2\text{O}$	0	to	10
50	$\text{K}_2\text{O}$	0	to	10

55

the sum of

	$H_2O$ (H = Li, Na, K)		
5		5	to 17
	CaO	0	to 20
	MgO	0	to 15
10			
	SrO	0	to 4
	BaO	0	to 4
15			
	ZnO	0	to 5
	TiO <sub>2</sub>	1	to 15
	ZrO <sub>2</sub>	0	to 8
20			
	Nb <sub>2</sub> O <sub>5</sub>	0	to 5
	and F <sup>-</sup>	0	to 5.

25 US specification 4590171 claims a frit essentially free from cadmium and lead, demonstrating good glass stability, a coefficient of thermal expansion (20°-300°C) between about  $58-62 \times 10^{-7}/^{\circ}\text{C}$ , a softening point between about 600-625°C, and excellent resistance to attack by acids found in foods and to attack by alkaline detergents, said frit consisting essentially, expressed in wt% on the oxide basis, of:

30			
	Li <sub>2</sub> O	3	to 4
	Na <sub>2</sub> O	0.75	to 3
35			
	BaO	3.5	to 9.5
	B <sub>2</sub> O <sub>3</sub>	14	to 17.5
40			
	Al <sub>2</sub> O <sub>3</sub>	6.75	to 8.75
	SiO <sub>2</sub>	48	to 55
	ZrO <sub>2</sub>	6.75	to 10.5
45			
	and F	3	to 4.

50 US specification 3871890 discloses a component for glazing low-expansion ceramic whiteware with a substantially non-porous, acid-resistant, opaque glaze, a substantially water-insoluble ceramic frit being substantially entirely in the vitreous state as frit particles, said frit after melting into a fluent vitreous state being thermally autocrystallisable to a low-expansion, semi-crystalline glass-ceramic glaze containing zirconia or zircon as one of the crystalline phases and having a coefficient of thermal expansion of less than  $5 \times 10^{-6}/^{\circ}\text{C}$ , said frit consisting essentially of:

55

	<u>Ingredient</u>	<u>Wt%</u>
	$\text{Li}_2\text{O}$	about 3 to 22%
5	$\text{MgO}$	about 0 to 6%, 0.74 part of $\text{MgO}$ replacing 1 part of $\text{Li}_2\text{O}$ when $\text{MgO}$ is used, but a minimum of 4% $\text{Li}_2\text{O} + \text{MgO}$ being present
10	$\text{Al}_2\text{O}_3$	about 17 to 38%
	$\text{SiO}_2$	about 26 to 70%, the subtotal sum of $\text{Li}_2\text{O}$ , $\text{MgO}$ , $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ being 70 to 90%
15	$\text{ZrO}_2$	about 6 to 25%
20	Flux	about 4 to 19%.

wherein said flux is selected from the group consisting of:  $\text{B}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{F}$ ,  $\text{PbO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{ZnO}$ ,  $\text{BaO}$  up to 5% or mixtures of same.

The present invention provides a glass flux composition consisting essentially in mol percent of 3.0-13.0 lithium oxide, 0.5-3.5 potassium oxide, 2.5-7.0 sodium oxide, 0.5-2.5 zinc oxide, 2.0-8.0 aluminium oxide, 15-30 boron oxide, 44-68 silica, 1.0-7.0 zirconium oxide, 0-4.0 calcium oxide, 0-3.0 lanthanum oxide, 0-1.0 other rare earth metal oxide, 0-1.0 yttrium oxide, 0-4.0 magnesium oxide, 0-4.0 strontium oxide, 0-4.0 titanium oxide, 0-10 phosphorus pentoxide, 0-1.5 lead oxide and 0-13.0 fluoride. The composition preferably comprises a frit.

The invention provides also an enamel composition consisting essentially by weight of 10-90% of the glass flux composition comprising a frit together with 10-90% pigment.

The invention provides also a cover flux composition comprising the glass flux composition comprising a frit, dispersed in a carrier material.

The invention also provides an article bearing on its surface the enamel composition which has been fired thereon.

The invention also provides an article bearing on its surface the cover flux composition which has been fired thereon.

The invention provides also a method of applying an enamel composition to an article, which method comprises applying the present enamel composition to the article and then firing the composition.

The invention provides also a method of applying a cover flux composition to an article, which method comprises applying the present cover flux composition to the article and then firing the composition.

The present glass flux composition is advantageously lead-free. By "lead-free" we mean that no lead has been included deliberately but a slight amount may have been picked up incidentally, for instance during processing in equipment previously used for lead-containing compositions. Preferably, the glass flux composition is lead-less, by which we mean that no lead has been included deliberately and no lead has been picked up incidentally. The present glass flux composition is also cadmium-free. It can readily be made into an enamel or cover flux composition which can readily be applied and fired. After firing, the enamel or cover flux composition has good chemical and mechanical resistance, for instance resistance to acids or alkalis, and has a good gloss making it particularly attractive.

The content of the present glass flux composition is expressed herein in mol percents. The weight percent contents depend on which if any other rare earth metal oxide is present. For these purposes, we count yttrium as not being a rare earth metal.

In a particular embodiment, the present glass flux composition consists essentially in mol percent of 3.0-11.5 lithium oxide, 0.5-3.5 potassium oxide, 2.5-5.0 sodium oxide, 0.5-4.0 calcium oxide, 0.5-2.5 zinc oxide, 2.0-7.5 aluminium oxide, 15-30 boron oxide, 44-68 silica, 1.0-5.0 zirconium oxide, 0-3.0 lanthanum oxide, 0-1.0 other rare earth metal oxide, 0-1.0 yttrium oxide, 0-4.0 magnesium oxide, 0-4.0 strontium oxide, 0-4.0 titanium oxide, 0-10 phosphorus pentoxide, 0-1.5 lead oxide and 0-8.0 fluoride.

The present glass flux composition preferably contains 7-10.2 mol percent lithium oxide. Its potassium oxide content is preferably 1.5-1.8 mol percent. Its sodium oxide content is preferably 3.4-4.0 mol percent. Its calcium oxide content is preferably 0.8-1.2 mol percent. Its zinc oxide content is preferably 1.0-1.3 mol percent. Its aluminium oxide content is preferably 4.3-5.5 mol percent. Its boron oxide content is preferably 18.8-22.5 mol percent. Its silica content is preferably 48-57 mol percent. Its zirconium oxide content is preferably 1.8-3.4 mol percent. For increased brightness of fired coatings based on it, the composition very desirably contains 0.1-3.0, especially 0.2-0.8, mol percent yttrium oxide. Its content of other rare earth metal oxide is preferably 0-0.4 mol percent. Its content of yttrium oxide is preferably 0-0.6 mol percent. Its content of magnesium oxide is preferably 0-1.5 mol percent. Its content of strontium oxide is preferably 0-1.5 mol percent. Its content of titanium oxide is preferably 0-3 mol percent. Its content of phosphorus pentoxide is preferably 0-6 mol percent. The composition preferably contains 0-7 mol percent fluoride; to avoid any possible pollution problem, however, fluoride is preferably avoided.

It can be seen that at most the composition contains much less lead than the usual lead-containing compositions. Preferably, the composition contains less than 0.2 mol percent lead oxide. It is especially preferred that it contains no added lead. It may pick up trace amounts of lead from the surroundings, for example from processing on equipment previously employed to process lead-containing compositions, but preferably steps are taken to avoid this.

Any rare earth metal oxide other than lanthanum oxide is preferably one or more, usually one, of praseodymium oxide, cerium oxide and neodymium oxide, especially neodymium oxide. Whatever the form of the cerium oxide (and in particular whether it is  $\text{CeO}_2$  or  $\text{Ce}_2\text{O}_3$ ), its content is calculated as  $\text{CeO}_2$ .

The flux composition can be made and used in conventional ways. The composition can be made by a process comprising admixing the ingredients. The ingredients can be introduced in the form of their oxides, or mixed oxides such as zirconium silicate or lithium aluminium silicate. Alternatively, ingredients can be introduced as compounds such as carbonates (for instance lithium carbonate) or nitrates (for instance potassium nitrate) which form the oxides during production. Any fluoride is preferably introduced as lithium fluoride, sodium fluoride or sodium fluosilicate. Any element, such as the lithium, sodium, or sodium and silicon, used to introduce the fluoride, counts also, calculated as oxide, towards any oxide content essential in the composition, as is conventional in the art. Any phosphorus pentoxide is preferably introduced as an ammonium or sodium phosphate, and again any element, such as the sodium, used to introduce the phosphorus pentoxide, counts also, calculated as oxide, towards any oxide content essential in the composition, as is conventional in the art. Advantageously, the flux composition comprises a frit, which can be prepared by a process comprising melting the ingredients together (for instance at 1200-1350 °C for 1-3 hours), quenching to form a solid glass and optionally granulating. The flux composition preferably consists of the frit. Alternatively, a frit of some of the ingredients can be admixed in powder form with the remainder of the ingredients to form the flux composition. Alternatively again, part of the flux composition can be incorporated while admixing a frit consisting essentially of the other ingredients with a pigment to form an enamel composition.

The present flux composition, generally the frit, usually has a melting temperature in the range 470-610 °C, preferably 500-580 °C. Its thermal expansion is usually in the range  $5.0-10.0 \times 10^{-6}/^\circ\text{C}$ , preferably  $6.0-8.0 \times 10^{-6}/^\circ\text{C}$ . Its refractive index is usually 1.51-1.57.

The present enamel or cover flux composition can be made and used in conventional ways. It can be made by admixing the ingredients, preferably by milling. The pigment employed in the enamel composition can be conventional. The enamel composition consists essentially by weight of 10-90% of the glass flux composition comprising the frit together with 10-90% of pigment, preferably 60-90% of the glass flux composition together with 10-40% pigment. The enamel composition is usually applied as a dispersion in a carrier material. The dispersion usually contains 60-75% by weight of the enamel composition. The cover flux composition usually comprises 60-75% by weight of the glass flux composition comprising the frit, dispersed in a carrier material. In either case, the carrier material can be an aqueous or organic medium; it can be thermoplastic; it can be infra-red drying or ultra-violet curing; all such types of media are known and can be employed in their known ways. The enamel or cover flux composition is preferably lead-free, especially lead-less.

The enamel or glass flux composition can be applied to an article in the usual way. For instance, the enamel composition can be applied by printing (for example screen printing) or spraying, and the cover flux composition can be applied by printing (for example screen printing). Either composition can be applied as a paste. The enamel composition can be applied directly to the article to be decorated with the enamel. Alternatively, the enamel composition can be used to form a transfer which in turn is applied to the article to be decorated with the enamel. The cover flux composition can be used to form a layer in a transfer containing an enamel decoration layer, so that after application of the transfer to an article, the cover flux

protects the underlying enamel decoration layer. In this way, the cover flux can inhibit the leaching of lead from an underlying lead-containing enamel layer. After application, the enamel or cover flux composition can be fired in the usual way, generally at 740-1270 °C. Usually for a standard firing cycle after application to glazed ceramic ware, the temperature is within the range 740-840 °C and the firing time is 5-7 hours, with the peak temperature being held for 0.8-1.3 hours. By "glazed" we mean that the article bears a fired glaze. Usually for a fast firing cycle after application to glazed ceramic ware, the firing temperature is within the range 740-950 °C and the firing time is 0.5-4 hours, with the peak temperature being held for 5-20 minutes.

The enamel or cover flux composition is preferably applied to ceramic ware; bone china, earthenware and porcelain can all be treated. The ceramic ware bearing the fired composition preferably bears also a fired glaze. The enamel or flux composition is preferably applied to glazed ceramic ware. In all cases, the glaze is preferably lead-free, especially lead-less. Advantageously, the ceramic ware is an article adapted to contact food. Preferably, the ceramic article is table-ware such as a plate.

The invention is illustrated by the following Examples. In the Examples, the lithium oxide was provided in the form of lithium carbonate, the zirconia as zirconium silicate, the boron oxide as boric acid, the alumina as alumina hydrate, the calcium oxide as calcium carbonate, the sodium oxide as sodium carbonate, the potassium oxide as potassium nitrate, and the fluoride as lithium fluoride up to the content of lithium in the composition with any remainder as sodium fluoride. The remaining ingredients were provided as such. The frits were prepared by melting the ingredients together in a crucible at 1200-1350 °C for 1 to 3 hours until a homogeneous mixture had been obtained, quenching the molten material in water, and drying. The frit was ground together with the pigment based on transition metal oxides at weight ratios of frit: pigment of 10:1 to 3.5:1 using a ball mill containing porcelain grinding medium for 16-20 hours to give the particle size distribution, measured on a Malvern laser particle sizer model 3600E type using as the dispersing agent 1g/litre sodium hexametaphosphate solution:

50% less than 5.8 microns

90% less than 16.8 microns

10% less than 1.5 microns

The ground material was dried, and sieved through a 75 micron mesh (0.075mm sieve aperture) to give the enamel composition. The enamel composition was dispersed in the commercial air-drying transfer-printing organic medium 63/537 available from Blythe Colours, Cresswell, England at weight ratios of powder to medium of 10:5-10:7 using a triple roll mill. The resultant paste was screen printed onto transfer sheets through a 90T screen (number count per cm). The sheets were covercoated using the commercial organic lacquer OPL 164 available from Blythe colours, Cresswell, England to obtain transfers. The transfers were applied, after soaking off the backing sheet, to china plates, porcelain plates and earthenware tiles, all previously glazed with lead-free glazes. The china was fired in a kiln whose temperature was raised at 150 °C per hour to a peak temperature of 780 °C, the china being held at this temperature for 1 hour before being allowed to cool naturally to ambient temperature. The porcelain was standardly fired in a kiln whose temperature was raised at 150 °C per hour to a peak temperature of 810 °C, the porcelain being held at this temperature for 45 minutes before being allowed to cool naturally to ambient temperature. The porcelain was fired in a fast firing cycle in a kiln whose temperature was raised at 32 °C per minute to a peak temperature of 950 °C, the porcelain being held at this temperature for 5 minutes before being allowed to cool naturally to 600 °C and then cooled by forced air to ambient temperature. The earthenware was fired in a kiln whose temperature was raised at 150 °C per hour to a peak temperature of 740 °C, the earthenware being held at this temperature for 1 hour before being allowed to cool naturally to ambient temperature. The gloss of fired enamels was assessed visually on a scale from A to E where A represents very glossy, C a good gloss and E matt. The colour strength of fired enamels was assessed visually on a scale from A to E where A represents very strong, C a good colour and E very weak. The acid resistance was assessed visually after immersing the article in 5% by volume acetic acid for 16 hours at ambient temperature, on a scale from A to E where A represents no evidence of attack and E very severe attack. The alkali resistance was assessed visually by immersing the article twice in a solution of 4g/litre of material consisting of sodium metasilicate (40% by weight), sodium carbonate (40% by weight) and sodium tripolyphosphate (20% by weight) in de-ionised water at 73 °C, on a scale from A to E where A represents no evidence of attack and E very severe attack.

## Examples 1-7

The following frits were prepared:

	Example 1		Example 2		Example 3		Example 4	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
K <sub>2</sub> O	2.32	1.60	2.33	1.56	2.33	1.57	2.32	1.60
Na <sub>2</sub> O	3.84	4.00	3.74	3.82	3.74	3.84	3.66	3.83
CaO	0.84	0.97	0.84	0.95	0.84	0.95	1.25	1.45
ZnO	1.46	1.16	1.46	1.14	1.46	1.14	1.45	1.16
Al <sub>2</sub> O <sub>3</sub>	6.06	3.86	5.91	3.67	7.87	4.91	6.86	4.37
B <sub>2</sub> O <sub>3</sub>	23.21	21.62	22.82	20.76	22.83	20.87	21.91	20.44
SiO <sub>2</sub>	55.52	59.92	54.28	57.21	52.96	56.10	51.80	55.98
ZrO <sub>2</sub>	4.76	2.51	4.60	2.37	3.95	2.04	3.94	2.07
Li <sub>2</sub> O	2.01	4.36	4.02	8.52	4.02	8.57	3.91	8.50
La <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	2.89	0.58
Y <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	-	-

	Example 5		Example 6		Example 7	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
K <sub>2</sub> O	2.20	1.54	2.19	1.57	2.31	1.59
Na <sub>2</sub> O	3.66	3.91	3.49	3.80	3.62	3.80
CaO	1.25	1.47	1.24	1.50	1.25	1.45
ZnO	1.45	1.18	1.44	1.20	1.45	1.16
Al <sub>2</sub> O <sub>3</sub>	5.70	3.70	4.72	3.12	5.86	3.74
B <sub>2</sub> O <sub>3</sub>	21.82	20.75	21.34	20.70	22.22	20.77
SiO <sub>2</sub>	50.51	55.63	49.62	55.76	51.52	55.80
ZrO <sub>2</sub>	3.76	2.02	3.75	2.05	3.91	2.07
Li <sub>2</sub> O	3.89	8.62	3.78	8.55	3.89	8.47
La <sub>2</sub> O <sub>3</sub>	5.75	1.17	8.42	1.75	-	-
Y <sub>2</sub> O <sub>3</sub>	-	-	-	-	3.97	1.15

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal expansion, ( $\times 10^{-6}$ ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
2	6.84	507	556	1.520
3	6.80	507	556	1.530

The frits were made into white (with cerium oxide), blue-green (with cobalt chromium pigment) and yellow (with praseodymium - zircon pigment) enamel compositions using the following weight ratios of frit to pigment:

White enamel 10:1

Blue-green enamel 5:1

Yellow enamel 6.6:1

The enamel compositions were applied to porcelain and fired in the standard cycle. Properties of the

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fired enamels were assessed as follows:

Frit of Example	Enamel Colour	Colour Strength	Gloss	Acid Resistance	Alkali Resistance
1	White Blue-Green Yellow	C C C	C- D C	A A A	E E E
2	White Blue-Green Yellow	C C C	C C C	A A A	A A B-
3	White Blue-Green Yellow	C C C	C D+ C	A A A	A B- B
4	White Blue-Green Yellow	C C C	C C- D+	A A A	B B+ B
5	White Blue-Green Yellow	C C C	D D D+	A A A	B B B
6	White Blue-Green Yellow	C C C	D- D- C	A A A	B- B- B
7	White Blue-Green Yellow	C C C	C- D+ C	A A A	A B B-

The frits of Examples 3 and 4 were made into a wider range of enamel compositions as follows:

Colour	Pigment Type	Frit:Pigment Weight Ratio
Orange	Sr Sb Ti	3.92 : 1
Iron Red	Fe	8 : 1
Blue	Co Al	4 : 1
Blue	Co Si	4 : 1
Brown	Fe Zn	6.67 : 1
Black	Cu Cr Mn	5 : 1

This wider range of enamel compositions was tested on all the ceramic wares. Properties of the fired enamels on porcelain after the standard firing cycle were assessed as follows:



Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
3	White	C	A	A
	Yellow	C	A	C-
	Orange	C	A	B
	Iron Red	C-	A	B-
	Blue (Co Al)	C	A	D
	Blue (Co Si)	C	A	B
	Blue-Green	C-	A	B
	Brown	C	A	B+
	Black	C	A	C+
4	White	C	A	A
	Yellow	C	A	B-
	Orange	C-	A	B
	Iron Red	D	A	B-
	Blue	D	A	C+
	Blue	D	C+	B
	Blue-Green	C-	A	B+
	Brown	C	A	A
	Black	C-	A	B

The results on porcelain after the fast firing cycle were very similar, though the enamel compositions based on the frit of Example 3 gave a better gloss than the enamel compositions based on the frit of Example 4. The cobalt-silica blue and the cobalt-alumina blue enamel compositions showed signs of attack by acid, the latter being more resistant.

The results after firing on china were excellent except for the cobalt-silica blue enamel compositions which were attacked by acid.

The results after firing on earthenware were excellent.

#### Examples 8 - 17

The following frits were prepared:

	Example 8		Example 9		Example 10		Example 11		Example 12	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
K <sub>2</sub> O	2.31	1.57	2.30	1.58	2.31	1.57	2.30	1.57	2.29	1.56
Na <sub>2</sub> O	3.72	3.85	3.63	3.78	3.72	3.84	3.70	3.85	3.69	3.82
CaO	1.11	1.27	1.11	1.27	1.25	1.43	1.24	1.43	1.24	1.42
ZnO	1.45	1.14	1.44	1.15	1.45	1.14	1.44	1.14	1.44	1.14
Al <sub>2</sub> O <sub>3</sub>	7.48	4.71	7.13	4.53	7.49	4.70	7.12	4.51	6.78	4.27
B <sub>2</sub> O <sub>3</sub>	22.50	20.75	22.30	20.72	22.53	20.73	22.54	20.89	22.34	20.63
SiO <sub>2</sub>	52.27	55.85	51.88	55.84	52.34	55.79	51.80	55.61	52.40	56.04
ZrO <sub>2</sub>	3.92	2.04	3.90	2.05	3.92	2.04	3.90	2.04	3.89	2.03
Li <sub>2</sub> O	3.99	8.57	3.98	8.61	3.99	8.56	3.97	8.58	3.96	8.52
La <sub>2</sub> O <sub>3</sub>	1.26	0.25	2.33	0.46	-	-	-	-	-	-
Y <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	-	-	1.97	0.56
Na <sub>2</sub> O	-	-	-	-	1.00	0.18	1.98	0.38	-	-

	Example 13		Example 14		Example 15		Example 16		Example 17	
	Vt%	Mol%	Vt%	Mol%	Vt%	Mol%	Vt%	Mol%	Vt%	Mol%
K <sub>2</sub> O	2.31	1.58	2.31	1.58	2.31	1.57	2.32	1.59	2.32	1.59
Na <sub>2</sub> O	3.71	3.87	3.71	3.86	3.72	3.85	3.64	3.79	3.64	3.80
CaO	0.83	0.96	0.83	0.96	0.83	0.95	0.83	0.96	0.83	0.96
ZnO	1.45	1.15	1.45	1.15	1.45	1.14	1.45	1.16	1.45	1.16
Al <sub>2</sub> O <sub>3</sub>	7.32	4.63	7.32	4.63	7.33	4.61	7.19	4.56	7.19	4.57
B <sub>2</sub> O <sub>3</sub>	22.52	20.87	22.35	20.71	22.24	20.49	23.58	21.90	25.11	23.37
SiO <sub>2</sub>	52.06	55.90	50.77	54.50	50.35	53.74	49.77	53.55	48.25	52.03
ZrO <sub>2</sub>	3.92	2.05	4.89	2.56	4.90	2.55	4.92	2.58	4.91	2.58
Li <sub>2</sub> O	3.99	8.62	4.86	9.68	4.99	10.72	4.07	9.54	4.04	9.55
La <sub>2</sub> O <sub>3</sub>	1.88	0.37	1.88	0.37	1.88	0.37	1.89	0.38	1.89	0.38

Properties were assessed follows:

Frit of Example	Coefficient of Thermal Expansion, (x10 <sup>-6</sup> ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
13	7.11	511	566	1.535
14	7.10	521	582	1.535
15	7.71	511	555	1.54
16	7.10	517	577	1.54
17	6.98	514	564	

The frits of Examples 13-17 were made up into white, yellow and blue-green enamel compositions in an analogous way to that described in Examples 1-7.

The enamel compositions were applied to porcelain and fired in the standard firing cycle and the fast firing cycle, and to china. Properties of the fired enamels on porcelain after the standard firing cycle were assessed as follows:

Frit of Example	Colour	Colour Strength	Gloss	Acid Resistance	Alkali Resistance
13	White Blue-Green Yellow	C C C-	C C C-	A A A	A- B D
14	White Blue-Green Yellow	C C C-	C C C	A A A	A- C+ D
15	White Blue-Green Yellow	C C C	C C C	A A A	A- C+ D+
16	White Blue-Green Yellow	C C C	C C C	A A A	A- B D
17	White Blue-Green Yellow	C C C	C C C	A A A	B C- D

The results on porcelain after the fast firing cycle were the same as those after the standard firing cycle.

The results after firing on china showed excellent gloss and acid resistance. The alkali resistance was very good except in the case of the yellow enamels, which showed slight attack.

The frits of Examples 15 and 16 were made into a wider range of enamel compositions in an analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and fired in the standard firing cycle and the fast firing cycle, and to china. The properties of the fired enamels on porcelain after the standard firing were assessed as follows:

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
15	White	C	A	B
	Blue-Green	C	A	B
	Yellow	C	A	D+
	Orange	C	A	A-
	Iron Red	C	A	C+
	Blue (Co Al)	C	A-	D
	Blue (Co Si)	C	D	D+
	Brown	C	A	C-
	Black	C	A-	B-
16	White	C	A	A
	Blue-Green	C	A	A-
	Yellow	C	A	D+
	Orange	C	A	A-
	Blue (Co Al)	C	A	D+
	Blue (Co Si)	C	B	C-
	Brown	C	A	B
	Black	C	A	B+

The results on porcelain after the fast firing cycle showed the same trends as those after the standard firing cycle, but the alkali resistance was slightly worse.

The results after firing on china were excellent. Only the yellow and cobalt-alumina blue enamel compositions showed slight attack.

#### Examples 18 - 20

The following frits were prepared:

	Example 18		Example 19		Example 20	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
K <sub>2</sub> O	2.33	1.60	2.33	1.60	2.34	1.62
Na <sub>2</sub> O	3.66	3.81	3.66	3.82	3.67	3.86
CaO	0.84	0.97	0.84	0.97	0.84	0.98
ZnO	1.46	1.16	1.46	1.16	1.47	1.17
Al <sub>2</sub> O <sub>3</sub>	7.24	4.59	8.22	5.21	8.26	5.27
B <sub>2</sub> O <sub>3</sub>	23.56	21.89	23.59	21.91	23.54	21.99
SiO <sub>2</sub>	49.28	53.03	49.34	53.09	48.28	52.25
ZrO <sub>2</sub>	5.93	3.11	4.95	2.60	5.96	3.15
Li <sub>2</sub> O	4.43	9.59	4.33	9.38	4.35	9.47
La <sub>2</sub> O <sub>3</sub>	1.27	0.25	1.27	0.25	1.27	0.25

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, ( $\times 10^{-6}$ ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
18	7.01	512	566	1.545
19	6.92	507	575	1.53
20	7.51	507	557	1.54

The frits were made into enamel compositions in an analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and fired in the standard firing cycle. Properties were assessed as follows:

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
18	White	C	A	C
	Blue-Green	C	A	C-
	Yellow	C	A	C-
19	White	C	A	A-
	Blue-Green	C	A	B
	Yellow	C	A	C-
	Orange	C	A	B-
	Iron Red	C	A	D+
	Blue (Co Al)	C	A-	E+
	Blue (Co Si)	C	C+	D-
	Brown	C	A	C-
20	Black	C	A	D+
	White	C	A	C
	Blue-Green	C	A	C
	Yellow	C	A	D-
	Orange	C	A	C+
	Iron-Red	C	A	D
	Blue (Co Al)	C	A-	E+
	Blue (Co Al)	C	B-	D-
	Brown	C	A	C
	Black	C	A	D-

## Examples 21 - 26

The following frits were prepared:

	Example 21		Example 22		Example 23		Example 24		Example 25		Example 26	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
K <sub>2</sub> O	2.32	1.60	2.32	1.60	2.31	1.56	2.29	1.53	2.33	1.60	2.33	1.61
Na <sub>2</sub> O	3.64	3.82	3.63	3.82	3.63	3.73	3.59	3.64	3.65	3.81	3.66	3.83
CaO	0.84	0.97	0.83	0.97	0.83	0.95	0.82	0.92	0.84	0.97	0.84	0.97
ZnO	1.46	1.16	1.45	1.16	1.45	1.14	1.44	1.11	1.95	1.55	2.44	1.94
Al <sub>2</sub> O <sub>3</sub>	9.16	5.83	10.11	6.46	8.15	5.09	8.07	4.97	8.20	5.21	8.22	5.23
B <sub>2</sub> O <sub>3</sub>	23.48	21.89	23.43	21.93	22.27	20.38	21.21	19.16	23.54	21.89	23.60	21.98
SiO <sub>2</sub>	48.61	52.51	47.75	51.80	48.91	51.87	48.42	50.67	48.97	52.76	48.35	52.17
ZrO <sub>2</sub>	4.92	2.59	4.91	2.60	4.90	2.54	4.85	2.48	4.94	2.59	4.95	2.60
Li <sub>2</sub> O	4.31	9.37	4.30	9.39	4.28	9.12	4.27	9.99	4.32	9.37	4.34	9.41
La <sub>2</sub> O <sub>3</sub>	1.26	0.25	1.26	0.25	1.26	0.25	1.24	0.24	1.26	0.25	1.27	0.25
P <sub>2</sub>	-	-	-	-	2.01	3.37	3.79	6.28	-	-	-	-

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, (x10 <sup>-6</sup> ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
21	7.25	498	536	1.54
22	7.07	493	542	1.525
23	7.09	475	532	1.53
24	7.29	445	512	1.53
25	7.16	497	537	1.535
26	7.49	500	551	1.54

The frits were made into enamel compositions in an analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and fired in the standard firing cycling. Properties were assessed as follows:

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
21	White Blue-Green Yellow	C C C	A A A	B- C- C
22	White Blue-Green Yellow	C C- C	A A A	C C- C
23	White Blue-Green Yellow	C C C	A A A	A- A- A-
24	White Blue-Green Yellow	C C C	A A A	A- A- A-
25	White Blue-Green Yellow	C C C	A A A	B B B
26	White Blue-Green Yellow	C C C	A A A	C+ B- C

## Examples 27 - 30

The following frits were prepared.

	Example 27		Example 28		Example 29		Example 30	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
Al <sub>2</sub> O <sub>3</sub>	7.20	4.55	7.20	4.55	7.19	4.55	7.20	4.55
B <sub>2</sub> O <sub>3</sub>	23.61	21.84	23.62	21.85	23.58	21.85	23.63	21.86
CaO	0.84	0.96	0.84	0.96	0.83	0.96	0.84	0.96
Ce <sub>2</sub> O <sub>3</sub>	1.14	0.22	0.57	0.11	-	-	-	-
CeO	0.36	0.13	0.18	0.07	-	-	-	-
K <sub>2</sub> O	2.32	1.59	2.32	1.59	2.32	1.59	2.32	1.59
La <sub>2</sub> O <sub>3</sub>	-	-	0.72	0.14	-	-	0.72	0.14
Li <sub>2</sub> O	4.41	9.51	4.41	9.51	4.40	9.51	4.42	9.52
Na <sub>2</sub> O	3.64	3.78	3.65	3.79	3.64	3.78	3.65	3.79
Pr <sub>2</sub> O <sub>3</sub>	-	-	-	-	1.66	0.32	0.71	0.14
SiO <sub>2</sub>	50.09	53.68	50.10	53.20	50.00	53.70	50.12	53.72
ZnO	1.46	1.15	1.46	1.15	1.45	1.15	1.46	1.15
ZrO <sub>2</sub>	4.92	2.57	4.92	2.57	4.91	2.57	4.93	2.57

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, ( $\times 10^{-6}$ ) per $^{\circ}\text{C}$	Transition Temperature, $^{\circ}\text{C}$	Melting Temperature, $^{\circ}\text{C}$	Refractive Index
27	7.17	515	567	1.535
28	7.17	515	557	1.545
29	7.20	511	565	1.54
30	7.52	512	561	1.55

The frits were made into enamel compositions in a analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and fired in the standard firing cycle. Properties were assessed as follows:

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
27	White Green Yellow	C+ C C+	A A A	C C- D
28	White Green Yellow	C C C	A A A	C+ C C+
29	White Green Yellow	C+ C C	A A A	A- A A-
30	White Green Yellow	C C C	A A A	A- A A

The results when fired on china were very good with only a slight discolouration of white enamel of frit 29.



## Examples 31 - 34

The following frits were prepared:

	Example 31		Example 32		Example 33		Example 34	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
$\text{Al}_2\text{O}_3$	8.05	4.89	7.94	4.76	8.00	4.97	8.00	4.93
$\text{B}_2\text{O}_3$	19.94	17.74	18.70	16.42	21.07	19.17	21.18	19.14
$\text{CaO}$	0.82	0.90	0.81	0.88	-	-	-	-
$\text{F}_2$	5.97	9.74	7.93	12.75	3.66	6.10	3.84	6.35
$\text{K}_2\text{O}$	2.29	1.50	2.25	1.46	3.59	2.42	2.32	1.55
$\text{La}_2\text{O}_3$	1.24	0.24	1.23	0.23	1.26	0.25	1.26	0.24
$\text{Li}_2\text{O}$	4.26	8.83	4.20	8.58	4.18	8.87	4.32	9.10
$\text{Na}_2\text{O}$	3.53	3.52	3.50	3.45	3.56	3.64	4.46	4.53
$\text{SiO}_2$	47.62	49.09	47.23	48.03	48.30	50.93	48.25	50.52
$\text{ZnO}$	1.43	1.09	1.41	1.06	1.45	1.13	1.45	1.12
$\text{ZrO}_2$	4.85	2.44	4.78	2.37	4.92	2.53	4.91	2.51

Properties were assessed as follows:

Frit of Example	Coefficient of thermal Expansion ( $\times 10^{-6}$ ) per $^{\circ}\text{C}$	Transition Temperature, $^{\circ}\text{C}$	Melting Temperature, $^{\circ}\text{C}$	Refractive Index
31	8.00	447	507	1.54
32	8.18	460	528	1.53
33	7.78	453	512	1.53
34	8.27	448	506	1.535

The frits were made into enamel compositions in an analogous way to that described in Examples 1-7. The enamels were applied to porcelain and china and fired in standard firing cycles. the properties were assessed as follows:

On Porcelain

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
31	White	C	A	A-
	Green	C	A	A-
	Yellow	C	A	A
32	White	C	A	A
	Green	C	A	A-
	Yellow	C	A	A
33	White	C-	A	A
	Green	C+	A	A
	Yellow	C-	A	A
34	White	C	A	A
	Green	C	A	A
	Yellow	C	A	A

The results on china were slightly better than the results obtained on porcelain.

Examples 35 - 38

The following frits were prepared:

	Example 35		Example 36		Example 37		Example 38	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
Al <sub>2</sub> O <sub>3</sub>	7.98	4.93	8.00	4.93	8.00	4.96	7.84	4.88
B <sub>2</sub> O <sub>3</sub>	21.13	19.14	21.19	19.14	21.02	19.09	21.02	19.18
F <sub>2</sub>	3.83	6.35	3.84	6.35	3.83	6.39	3.83	6.41
CaO	-	-	0.42	0.47	-	-	-	-
K <sub>2</sub> O	3.00	2.01	2.32	1.55	2.31	1.55	2.31	1.56
La <sub>2</sub> O <sub>3</sub>	1.26	0.24	1.26	0.24	1.26	0.24	1.26	0.25
Li <sub>2</sub> O	4.31	9.10	4.32	9.10	4.32	9.14	4.32	9.18
Na <sub>2</sub> O	4.00	4.10	4.01	4.07	4.46	4.55	4.37	4.47
SiO <sub>2</sub>	48.13	50.52	48.27	50.51	47.46	49.94	46.72	49.39
ZnO	1.45	1.12	1.45	1.12	1.45	1.13	1.45	1.13
ZrO <sub>2</sub>	4.90	2.51	4.91	2.51	5.89	3.02	6.87	3.54

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, ( $\times 10^{-6}$ ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
35	7.77	447	512	1.54
36	7.64	461	522	1.545
37	8.04	449	510	1.535
38	7.99	458	524	1.54

The frits were made into enamel compositions in an analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and china and were fired in the standard firing cycles. Properties were assessed as follows:

#### Assessment Results on Porcelain

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
35	White Green Blue	C C C	A A A	A B D
36	White Green Blue	C+ C+ C+	A A A	A A C
37	White Green Blue	C- C C	A A A	B A C
38	White Green Blue	C C C+	A A A	B B D

On china good results for alkali and acid resistance were obtained.

Examples 39 - 41

The following frits were prepared:

	Example 39		Example 40		Example 41	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
Al <sub>2</sub> O <sub>3</sub>	4.98	3.16	7.93	5.21	11.77	7.86
B <sub>2</sub> O <sub>3</sub>	18.72	17.37	21.76	20.94	15.42	15.09
CaO	1.02	1.18	0.88	1.05	0.88	1.07
K <sub>2</sub> O	1.95	1.34	2.32	1.65	2.94	2.12
La <sub>2</sub> O <sub>3</sub>	3.60	0.71	2.85	0.59	2.85	0.60
Li <sub>2</sub> O	3.37	7.28	2.75	6.16	5.61	12.78
Na <sub>2</sub> O	2.91	3.03	6.00	6.48	4.47	4.91
SiO <sub>2</sub>	58.81	63.22	47.67	53.15	41.03	46.52
ZnO	1.01	0.81	1.79	1.47	2.56	2.14
ZrO <sub>2</sub>	3.61	1.89	6.04	3.29	12.46	6.89

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, (x10 <sup>-6</sup> ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
39	6.63	525	584	1.53
40	7.44	509	571	1.54
41	9.21	511	565	1.56

The frits were made into enamel compositions in an analogous way to that described in Examples 1-7. The enamels were applied to porcelain and china and were fired in standard firing cycles.

Assessment Results on Porcelain

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
39	White	C	A	B
	Green	C	A	A
	Yellow	C	A	A
40	White	C	A	B
	Green	C	A	B
	Yellow	C	A	A
41	White	C	A	A
	Green	C	A	A
	Yellow	C	A	A

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The results on china all showed excellent acid and alkali resistance.

## Examples 42 - 46

The following frits were prepared.

	Example 42		Example 43		Example 44		Example 45		Example 46	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
Al <sub>2</sub> O <sub>3</sub>	8.02	5.20	4.25	2.16	4.25	2.69	11.92	7.86	11.61	7.80
B <sub>2</sub> O <sub>3</sub>	22.06	20.93	16.68	15.00	16.30	14.97	15.56	15.02	15.30	15.05
CaO	0.84	0.98	0.84	0.93	0.84	0.95	0.84	1.00	0.83	1.02
K <sub>2</sub> O	2.33	1.64	3.16	2.10	1.67	1.13	3.00	2.13	1.50	1.09
La <sub>2</sub> O <sub>3</sub>	2.89	0.59	3.06	0.59	3.07	0.60	2.88	0.59	2.89	0.61
Li <sub>2</sub> O	4.11	9.09	5.60	11.73	2.91	6.22	5.20	11.70	2.70	6.20
Na <sub>2</sub> O	3.56	3.79	4.88	4.93	2.53	2.61	4.58	4.97	2.38	2.63
SiO <sub>2</sub>	43.17	52.95	57.30	59.70	64.34	68.46	44.34	49.60	51.27	58.44
ZnO	1.94	1.58	0.96	0.74	0.97	0.76	2.66	2.20	2.66	2.24
ZrO <sub>2</sub>	6.07	3.25	3.27	1.66	3.12	1.61	9.00	4.91	8.85	4.92

Properties were assessed as follows:

Frit of Example	Coefficient of Thermal Expansion, (x10 <sup>-6</sup> ) per °C	Transition Temperature, °C	Melting Temperature, °C	Refractive Index
42	7.12	514	567	1.54
43	8.48	510	558	1.545
44	6.52	533	608	1.54
45	8.70	506	563	1.545
46	6.17	539	604	1.535

The frits were made into enamel compositions in an aqueous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and china and were fired in standard firing cycles.

Assessment Results on Porcelain

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
42	White	C	A	A
	Green	C	A	A
	Yellow	C	A	A
43	White	C	A	B
	Green	C	A	B
	Yellow	C	A	B
44	White	C	A	B
	Green	C	A	A
	Yellow	C	A	A
45	White	C	A	A
	Green	C	A	B
	Yellow	C	A	B
46	White	C	A	B
	Green	C	A	C
	Yellow	C	A	C

On china, excellent results were obtained for both acid and alkali resistance in all cases.

The frit of Example 42 was made into a wider range of enamel composition in an analogous way to that described in Examples 1-7. The enamel compositions were applied to porcelain and china and fired in standard firing cycles.

The results on porcelain were assessed as follows:

Frit of Example	Colour	Gloss	Acid Resistance	Alkali Resistance
42	White	C	A	A
	Blue Green	C	A	A
	Yellow	C	A	A
	Orange	C-	A	B
	Iron Red	C+	A	C
	Blue (Co Al)	C	A	C
	Blue (Co Si)	C	A	D
	Brown	C	A	B
	Black	C+	A	B

On china, good alkali and acid resistance was observed for all enamel compositions with the exception of the Iron Red which showed slight attack on alkali testing.

# Claims

1. A glass flux composition consisting essentially in mol percent of 3.0-13.0 lithium oxide, 0.5-3.5 potassium oxide, 2.5-7.0 sodium oxide, 0.5-2.5 zinc oxide, 2.0-8.0 aluminium oxide, 15-30 boron oxide, 44-68 silica, 1.0-7.0 zirconium oxide, 0-4.0 calcium oxide, 0-3.0 lanthanum oxide, 0-1.0 other rare earth metal oxide, 0-1.0 yttrium oxide, 0-4.0 magnesium oxide, 0-4.0 strontium oxide, 0-4.0 titanium oxide, 0-10 phosphorus pentoxide, 0-1.5 lead oxide and 0-13.0 fluoride.
2. A glass flux composition consisting essentially in mol percent of 3.0-11.5 lithium oxide, 0.5-3.5 potassium oxide, 2.5-5.0 sodium oxide, 0.5-4.0 calcium oxide, 0.5-2.5 zinc oxide, 2.0-7.5 aluminium oxide, 15-30 boron oxide, 44-68 silica, 1.0-5.0 zirconium oxide, 0-3.0 lanthanum oxide, 0-1.0 other rare earth metal oxide, 0-1.0 yttrium oxide, 0-4.0 magnesium oxide, 0-4.0 strontium oxide, 0-4.0 titanium oxide, 0-10 phosphorus pentoxide, 0-1.5 lead oxide and 0-8.0 fluoride.
3. A composition according to claim 1 or 2 which contains 0.1-3.0 mol percent lanthanum oxide.
4. A composition according to any one of claims 1 - 3 which comprises a frit.
5. A process for preparing a glass flux composition claimed in any one of the preceding claims, which process comprises admixing its ingredients.
6. A process for preparing a glass flux composition claimed in claim 4, which process comprises melting the ingredients of the frit together and quenching the melt to form a glass.
7. An enamel composition consisting essentially by weight of 10-90% of the composition claimed in claim 4 together with 10-90% pigment.
8. A process for preparing an enamel composition claimed in claim 7, which process comprises admixing its ingredients.
9. A cover flux composition comprising the composition claimed in claim 4 dispersed in a carrier material.
10. A process for preparing a cover flux composition claimed in claim 9, which process comprises dispersing the glass flux composition claimed in claim 4 in the carrier material.
11. An article bearing on its surface an enamel or cover flux composition claimed in claim 7 or 9 which has been fired thereon.
12. An article according to claim 11 which is a ceramic article.
13. A method of applying an enamel or cover flux composition to an article, which method comprises applying a composition claimed in claim 7 or 9 to the article and then firing the composition.

## Patentansprüche

1. Glasflußzusammensetzung bestehend im wesentlichen, ausgedrückt in Mol%, aus 3,0 bis 13,0 Lithiumoxid, 0,5 bis 3,5 Kaliumoxid, 2,5 bis 7,0 Natriumoxid, 0,5 bis 2,5 Zinkoxid, 2,0 bis 8,0 Aluminiumoxid, 15 bis 30 Boroxid, 44 bis 68 Siliziumdioxid, 1,0 bis 7,0 Zirkoniumoxid, 0 bis 4,0 Calciumoxid, 0 bis 3,0 Lanthanoxid, 0 bis 1,0 anderen Selten-Erd-Metalloxiden, 0 bis 1,0 Yttriumoxid, 0 bis 4,0 Magnesiumoxid, 0 bis 4,0 Strontiumoxid, 0 bis 4,0 Titanoxid, 0 bis 10 Phosphorpentoxid, 0 bis 1,5 Bleioxid und 0 bis 13,0 Fluorid.
2. Glasflußzusammensetzung im wesentlichen bestehend aus, ausgedrückt in Mol%, 3,0 bis 11,5 Lithiumoxid, 0,5 bis 3,5 Kaliumoxid, 2,5 bis 5,0 Natriumoxid, 0,5 bis 4,0 Calciumoxid, 0,5 bis 2,5 Zinkoxid, 2,0 bis 7,5 Aluminiumoxid, 15 bis 30 Boroxid, 44 bis 68 Siliziumdioxid, 1,0 bis 5,0 Zirkoniumoxid, 0 bis 3,0 Lanthanoxid, 0 bis 1,0 anderen Selten-Erd-Metalloxiden, 0 bis 1,0 Yttriumoxid, 0 bis 4,0 Magnesiumoxid, 0 bis 4,0 Strontiumoxid, 0 bis 4,0 Titanoxid, 0 bis 10 Phosphorpentoxid, 0 bis 1,5 Bleioxid und 0 bis 8,0 Fluorid.

3. Zusammensetzung nach Anspruch 1 oder 2, die 0,1 bis 3,0 Mol% Lanthanoxid enthält.
4. Zusammensetzung nach einem der Ansprüche 1 bis 3, die eine Fritte umfaßt.
5. Verfahren zur Herstellung einer Glasflußzusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Verfahren umfaßt, daß man die Inhaltsstoffe vermischt.
6. Verfahren zur Herstellung einer Glasflußzusammensetzung nach Anspruch 4, wobei das Verfahren umfaßt, daß man die Inhaltsstoffe der Fritte miteinander verschmilzt und die Schmelze abschreckt unter Bildung eines Glases.
7. Emailzusammensetzung im wesentlichen bestehend aus, bezogen auf Gewicht, 10 bis 90% der in Anspruch 4 beanspruchten Zusammensetzung zusammen mit 10 bis 90% Pigment.
8. Verfahren zur Herstellung einer Emailzusammensetzung nach Anspruch 7, wobei das Verfahren umfaßt, daß man die Inhaltsstoffe vermischt.
9. Deckflußzusammensetzung umfassend die Zusammensetzung von Anspruch 4 dispergiert in einem Trägermaterial.
10. Verfahren zur Herstellung einer Deckflußzusammensetzung nach Anspruch 9, wobei das Verfahren umfaßt, daß man die Glasflußzusammensetzung von Anspruch 4 in dem Trägermaterial dispergiert.
11. Gegenstand, der auf seiner Oberfläche eine Email- oder Deckflußzusammensetzung nach Anspruch 7 oder 9 trägt, die darauf gebrannt wurde.
12. Gegenstand nach Anspruch 11, der ein Keramikgegenstand ist.
13. Verfahren zum Auftragen einer Email- oder Deckflußzusammensetzung auf einen Gegenstand, wobei das Verfahren umfaßt, daß man eine Zusammensetzung nach Anspruch 7 oder 9 auf den Gegenstand aufträgt und dann die Zusammensetzung brennt.

#### Revendications

1. Composition de fondant vitreux contenant essentiellement, en pourcentage molaire, 3,0 à 13,0 % d'oxyde de lithium, 0,5 à 3,5 % d'oxyde de potassium, 2,5 à 7,0 % d'oxyde de sodium, 0,5 à 2,5 % d'oxyde de zinc, 2,0 à 8,0 % d'oxyde d'aluminium, 15 à 30 % d'oxyde de bore, 44 à 68 % de silice, 1,0 à 7,0 % d'oxyde de zirconium, 0 à 4,0 % d'oxyde de calcium, 0 à 3,0 % d'oxyde de lanthane, 0 à 1,0 % d'un autre oxyde alcalino-terreux, 0 à 1,0 % d'oxyde d'yttrium, 0 à 4,0 % d'oxyde de magnésium, 0 à 4,0 % d'oxyde de strontium, 0 à 4,0 % d'oxyde de titane, 0 à 10 % de pentoxyde de phosphore, 0 à 1,5 % d'oxyde de plomb et 0 à 13,0 % de fluorure.
2. Composition de fondant vitreux contenant essentiellement, en pourcentage molaire, de 3,0 à 11,5 % d'oxyde de lithium, 0,5 à 3,5 % d'oxyde de potassium, 2,5 à 5,0 % d'oxyde de sodium, 0,5 à 4,0 % d'oxyde de calcium, 0,5 à 2,5 % d'oxyde de zinc, 2,0 à 7,5 % d'oxyde d'aluminium, 15 à 30 % d'oxyde de bore, 44 à 68 % de silice, 1,0 à 5,0 % d'oxyde de zirconium, 0 à 3,0 % d'oxyde de lanthane, 0 à 1,0 % d'un autre oxyde alcalino-terreux, 0 à 1,0 % d'oxyde d'yttrium, 0 à 4,0 % d'oxyde de magnésium, 0 à 4,0 % d'oxyde de strontium, 0 à 4,0 % d'oxyde de titane, 0 à 10 % de pentoxyde de phosphore, 0 à 1,5 % d'oxyde de plomb et 0 à 8,0 % de fluorure.
3. Composition selon la revendication 1 ou 2, qui contient 0,1 à 3,0 moles pour cent d'oxyde de lanthane.
4. Composition selon l'une des revendications 1 à 3, qui forme une fritte.
5. Procédé de préparation d'une composition de fondant vitreux selon l'une quelconque des revendications précédentes, comprenant le mélange de ses ingrédients.



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6. Procédé de préparation d'une composition de fondant vitreux selon la revendication 4, qui comprend la fusion des ingrédients de la fritte et le refroidissement de la matière fondue afin qu'elle forme un verre.
- 5 7. Composition d'émail contenant essentiellement 10 à 90 % en poids de la composition selon la revendication 4 avec 10 à 90 % d'un pigment.
8. Procédé de préparation d'une composition d'émail selon la revendication 7, qui comprend le mélange de ses ingrédients.
- 10 9. Composition de couverte comprenant la composition de la revendication 4 dispersée dans un matériau formant un véhiculeur.
10. Procédé de préparation d'une composition de couverte selon la revendication 9, qui comprend la dispersion de la composition de fondant vitreux de la revendication 4 dans un véhiculeur.
- 15 11. Article portant en surface une composition d'émail ou de couverte selon la revendication 7 ou 9, cuite sur l'article.
12. Article selon la revendication 11, constitué d'un article céramique.
- 20 13. Procédé d'application d'une composition d'émail ou de couverte d'un article, le procédé comprenant l'application d'une composition selon la revendication 7 ou 9 à l'article, puis la cuisson de la composition.

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